High-Resolution Pulsed Field Ionization Photoelectron-Photoion Coincidence Study of NH_3: Accurate 0 K Dissociation Threshold for NH_2^+

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INTRODUCTION

As a fundamental molecule of both chemical and biological interest, the dissociation threshold of NH_3

$$NH_3 + h\nu \rightarrow NH_2^+ + H + e \quad (1)$$

has been studied for decades. Using the newly developed pulsed field ionization photoelectron-photoion coincidence (PFI-PEPICO) technique, formation of NH_2^+ from photo-dissociation from NH_3 by highly monochromotized synchrotron radiation has been investigated near the dissociation threshold. The PFI-PEPICO time of fight (TOF) spectra reveal that the fragmentation of NH_3 in high-n Rydberg states occurs at energies above the dissociation threshold prior to pulsed field ionization. Simulation of the breakdown diagram with respect to the 'cold' part and the overall abundance of parent and daughter ions result in an identical disappearance energy. Thereby an unambiguous measure of 0 K ion dissociation threshold for NH_2^+ from NH_3 is 15.7650 ± 0.0010 eV.

EXPERIMENT

All measurements were made using the newly developed PFI-PEPICO apparatus and dispersed multibunch synchrotron radiation from the ALS. In the multibunch operation, the ALS period (656 ns) consists of 272 micro-VUV bunch (bunch width = 50 ps, separation of adjacent bunches = 2 ns) followed by a dark gap (light off period) of 112 ns. Because of narrower dark gap provided by ALS than previously, the quality of the spectrum is somehow discounted. In this study, the PFI pulse (height =7.3 V/cm, width=200 ns) was applied approximately 10 ns after the start of the dark gap. A dc field of 0.2 V/cm is maintained across the interaction region to sweep prompt electrons from the ionization region prior to the application of the electric field pulse for Stark ionization. The PFI-PE selection was achieved by employing the electron TOF scheme. The ion PFI-PEPICO TOF spectra were recorded using a multichannel scaler triggered by the detection of an electron.

The photon energy ($h\nu$) calibration was achieved using the PFI-PE bands for $Ne^+(^2P_{3/2})$,$Ar^+(^2P_{3/2})$ and $Xe^+(^2P_{3/2})$ recorded under the same experimental conditions before and after each scan. This calibration procedure assumes that the Stark shift for ionization thresholds of NH_3 and the rare gases are identical. On the basis of the measured PFI-PE band for $Ar^+(^2P_{3/2})$, we estimate that the ion-energy selection achieved here is ≈1.0 meV (FWHM). The NH_3 is purified anhydrous compressed gas. At the stagnation pressure of 600 torr, NH_3 is supersonically expanded to main chamber, maintaining a stable pressure of 8×10^{-7} torr.

RESULTS AND DISCUSSION

A. PFI-PEPICO TOF spectrum

We have obtained PFI-PEPICO TOF spectra for NH_2^+ and NH_3^+ in the $h\nu$ region of 15.65-15.85 eV, which is near the NH_3^+ dissociation threshold. Selected PFI-PEPICO TOF spectra are depicted in Fig.1. These spectra have been background corrected.

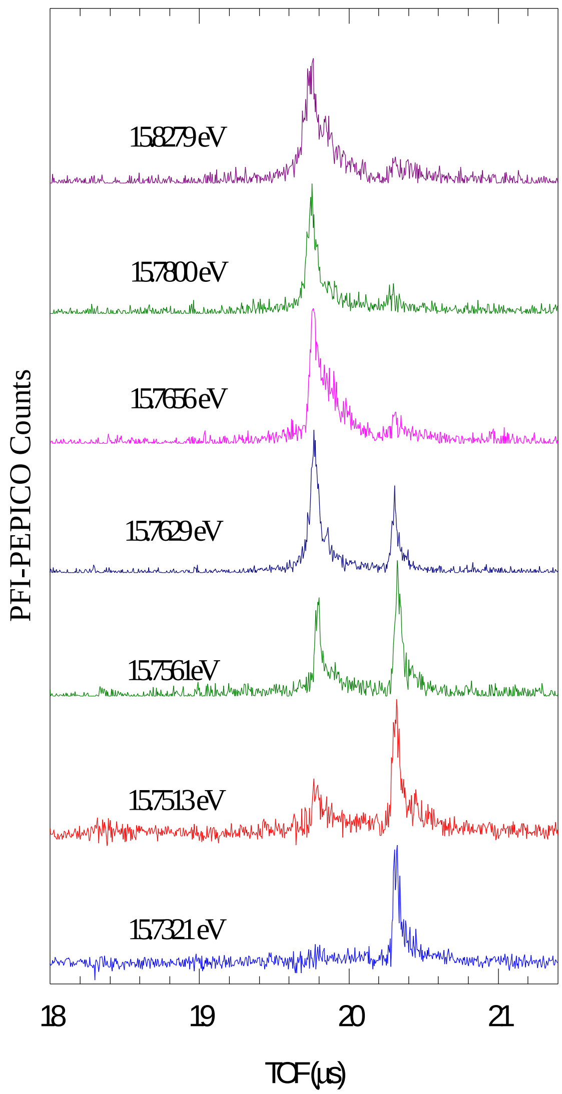

Figure 1.PFI-PEPICO TOF spectra for NH_2^+ and NH_3^+ in the hν range of 15.7321-15.7696 eV. The TOF peaks centered at 19.78 and 20.34 µs are due to NH_2^+ and NH_3^+, respectively. The hν values associated with individual spectra are indicated on the left-hand side of the spectra

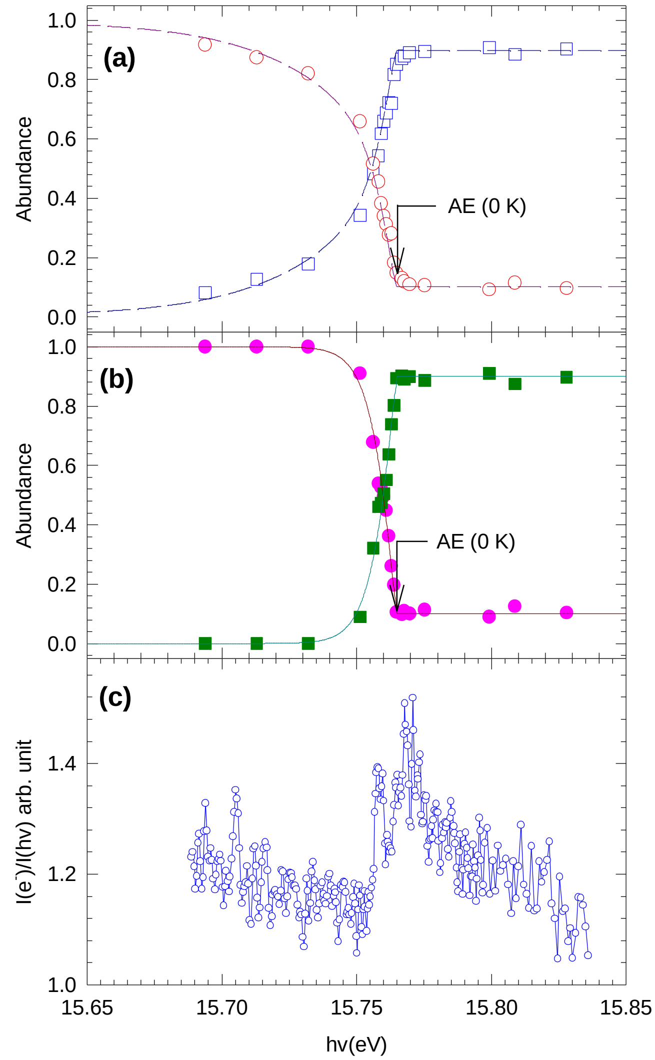

Figure 2. Breakdown curves of NH_2^+ and NH_3^+ in the hν range of 15.65-15.85 eV. The experimental fractional abundances for NH_2^+ and NH_3^+ obtained based on the entire daughter ion signal are (O) and (ÿ) in panel (a), whereas those using only the cold daughter ion signal are indicated as (●) and (■) in panel (b), respectively. The lines are simulations curves: (– –) 60 K ensemble with 10% thermal (298 K) background, panel (a) and (—) 60 K ensemble, panel (b). See the text. Panel (c): The PFI-PE spectrum of NH_3^+ near the dissociation threshold.

B. Simulation of the breakdown diagram

To derive the relative abundance of parent ions verses daughter ions, Gaussian fit has been applied to all the PFI-PEPICO TOF spectra. Due to the efficient rotational cooling of NH_3 achieved by the supersonic expansion, the 'cold' breakdown curves thus obtained are very sharp as indicated by open and solid squares for the respective fractional abundances of NH_2^+ and NH_3^+ shown in Fig. 2b. We have also constructed the breakdown curves for NH_2^+ and NH_3^+ [see open and solid circles, respectively, in Fig. 2a] by including the total 'hot' and 'cold' NH_2^+ signals. The breakdown diagram was fitted by assuming that the ion energy resolution is infinitely narrow and that the broadening of the breakdown diagram is due solely to the thermal energy in the NH_3 molecule. The solid lines in Figure 2 were obtained by convoluting this thermal energy distribution with a step function at the dissociation limit (AE). By assuming a temperature of 60K for NH_3 in the molecular beam, we have obtained an excellent simulation (solid lines, Fig. 2b) of the 'cold' breakdown curves, yielding a value of 15.7650±0.0010 eV for the 0 K dissociation threshold of NH_2^+ from NH_3. The dashed lines in Fig.2a are calculated breakdown curves assuming 10% thermal background (298K) in addition to the 60 K cold beam discussed above.

C. Dissociation mechanism

As expected, although the shapes and cross-over points of the two sets of break down curves obtained by including and excluding the dissociation of 'hot' NH_3 sample are quite different, the disappearance energies for the parent NH_3^+ are identical. We emphasize that in order for this feature to serve as a true measure of the ion dissociation threshold, the dissociation reaction must be prompt, i.e., the dissociation lifetime of the excited parent species is much shorter then the time scale ($\approx 10^{-7}$ s) of the experiment.

For the decay of NH_3^+, there are two important competing decay channels: autoionization and fragmentation. If the ion core NH_3^+ of NH_3^* is dissociative with a lifetime shorter than the delay time between the excitation micro-VUV pulse for the formation of NH_3^* and the electric field pulse for PFI, a viable mechanism for the formation of NH_2^+ from NH_3^* is

$$NH_3 + h\nu \rightarrow NH_3^* \rightarrow NH_2^* + H \rightarrow NH_2^+ + e^- + H \quad (2)$$

According to this mechanism, NH_3^* first undergoes prompt dissociation to form NH_2^* + H. The subsequent PFI of NH_2^* results in the formation of NH_2^+ and a PFI-PE. A strong evidence for the above mechanism is the observation of the "step" in the PFI-PE spectrum near the dissociation threshold. Fig 3 shows the PFI-PE for NH_3^+ in the energy range of 15.68-15.84 eV. The significant intensity jump of the PFI-PE near the dissociation threshold can be viewed as a strong support and be interpreted by that the lifetime for $NH_2^*(n)$ is longer than that for $NH_3^*(n)$.

D. Thermalchemical quantities

Taking into account the experimental uncertainties, the dissociation threshold (15.7650±0.0010 eV) for NH_3^+ from NH_3 determined here is consistent with values obtained in previous studies. However, the value obtained here is characterized by a significantly higher accuracy. Using the 0 K dissociation threshold for NH_2^+ from NH_3 determined here and the well-known IE of NH_3, we obtained $D_0(H\text{-}NH_2^+)$ = 5.5786±0.0010 eV. In addition, using the well-established values for $\Delta H^\circ_{f0}(NH_3)$ and $\Delta H^\circ_{f0}(H)$, according to process (1), we obtained obtain $\Delta H^\circ_{f0}(NH_2^+)$ = 1265.94±0.40 kJ/mol. We note that the accuracy of the latter value is now limited by the $\Delta H^\circ_{f0}(NH_3)$.

REFERENCE

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 for the Lawrence Berkeley National Laboratory and Contract No. W-7405-Eng-82 for the Ames Laboratory.

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